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(54) Title: EXPANDABLE BEADS BASED ON A POLYMER OF A VINYLAROMATIC COMPOUND CONTAINING BLOWING AGENT AND PLASTICIZER

(57) Abstract

The invention relates to expandable beads based on a polymer of a vinylaromatic compound having a weight average molecular weight (M_w) in the range of 180,000 to 500,000 and containing a blowing agent and a plasticizer in an amount of 0.1 up to 4 wt.% (as calculated on the total weight of the beads), wherein the plasticizer is an oligomer of styrene and/or alpha-methylstyrene having a number-average molecular weight (M_n) in the range of 200 to 2,000; a process for preparing these expandable beads, and articles of expanded beads, obtainable by expanding and fusing these beads.

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EXPANDABLE BEADS BASED ON A POLYMER OF A VINYLAROMATIC COMPOUND CONTAINING BLOWING AGENT AND PLASTICIZER

The invention relates to expandable beads based on a polymer of a vinylaromatic compound containing a blowing agent and a plasticizer. Moreover, the invention relates to a process for preparing these expandable beads, and articles of expanded beads, obtainable by expanding and fusing these beads.

Expandable beads, such as for instance the range of expandable polystyrene grades sold by Shell under the trademark "STYROCELL", find many different uses. Of particular interest are the grades for high strength, low density applications (e.g., the "STYROCELL M" grades) that find use in low density block or continuous board mouldings, large boxes and medium density insulating boards, blocks for veneer cutting, higher strength contour mouldings, packages with wall thickness above 10 mm, fish boxes, floor units, etc.

Expandable beads in the market place are mainly judged by three performance criteria, namely expandability, strength (fusion) and dimensional stability in the form of a short pressure-decay time (i.e., the minimum time the foamed article needs to remain in the mould to avoid warping, etc.). Both high ratings for strength (of the moulded article) and expandability (of the expandable beads) are desired. Moreover, it is preferred that articles of satisfactory strength may be prepared by expanding the expandable beads at low steam pressures, for instance of about 0.6 bar gauge. Finally, the pressure-decay time, which affects the overall cycle time, should be as short as possible.

In the art, it is known to use a plasticizer, such as for instance white oil and cyclohexane, to improve expansion at low steam pressures. Use of white oil, however, however, reduces the strength at ordinary steam pressures, whereas at low steam pressures, the strength is hardly improved. The operating window is thus very small. Cyclohexane is a better plasticizer, improving expansion and strength at low steam pressures. Unfortunately, cyclohexane is not approved for food contact applications in the European market.

US patents Nos. 4,525,484 and 4,459,373 disclose expandable beads based on polystyrene respectively poly-para-methylstyrene having a weight average molecular weight (M_w) in the range of 130,000 to 180,000 that are produced by polymerizing (para-methyl)styrene in aqueous suspension in the presence of blowing agents and of chain transfer agents or (para-methyl)styrene oligomers. These oligomers have a number-average molecular weight (M_n) from 500 to 5,000, preferably 800 to 2,000 and are added at a conversion of from 0 to 90%. As is shown in these patent specifications, low densities are attainable at high troughputs without adverse effect on the dimensional stability of the foamed articles when using expandable beads prepared in the presence of 1-1.5 %wt of a styrene oligomer that has an M_n of 1,200. On the other hand, the patent specifications are silent on improvement in strength at low steam pressures. Indeed, when this oligomer is used in regular grade expandable beads (M_w in the range of 130,000 to 180,000) as in Comparative Example F set out hereinafter, hardly any improvement in strength is found.

The inventors surprisingly found that, by use of these oligomers in grades of expandable beads based on a polymer of a vinylaromatic compound having a weight average molecular weight (M_w) in the range of 180,000 to

500,000, the afore-mentioned performance criteria could be substantially improved. Accordingly, the invention provides expandable beads based on a polymer of a vinylaromatic compound having a weight average molecular weight (M_w) in the range of 180,000 to 500,000 containing a blowing agent and a plasticizer in an amount of 0.1 up to 4 %wt (as calculated on the total weight of the beads), wherein the plasticizer is an oligomer of styrene and/or alpha-methylstyrene having a number-average molecular weight (M_n) in the range of 200 to 2,000. (The molecular weights as determined by Gel Permeation Chromatography).

Preferably, the expandable beads are based on polymers of styrene and/or alpha-methylstyrene, more preferably polystyrene (so-called "EPS"). However, the invention may also be applied using expandable beads that are based on copolymers of styrene and a copolymerizable monomer. The more common polymers having an M_w in the range of 185,000 to 300,000 are preferred.

The plasticizer suitably has an M_n in the range of 200 to 1,200, more suitably in the range of 500 to 900. The latter are preferably used in an amount of 1 up to 3 %wt, although more or less may also be used.

Blowing agents typically used for preparing the expandable beads comprise volatile (cyclo)hydrocarbons, halogenated hydrocarbons and other volatile organic compounds. In particular, pentane is a common blowing agent. It is typically used in an amount of 5.0 to 12 %wt. However, there is a concern for the presence of these volatile compounds in the atmosphere. Hence, the grade of expandable beads having a low content of blowing agent, e.g., containing 3 to 4.9 %wt, is increasing in popularity.

The invention also relates to the process for preparing these new expandable beads, by polymerizing the

vinylaromatic compound in aqueous suspension in the presence of the plasticizer and adding the blowing agent to the suspension before, during and/or after the polymerization. Suitably a radical initiator is used. The polymerization may also be initiated thermally, e.g., when styrene is the (co)monomer. Details with respect to the initiator and other process features are well known in the art.

Finally, the invention also relates to articles of expanded beads of a polymer of vinylaromatic compounds, obtainable by heating the new expandable beads in a mould at a temperature above the boiling point of the blowing agent and the softening point of the polymer. By heating the new beads, they expand and fuse. These articles have low density (due to the large expandability of the expandable beads) combined with excellent strength, and may be prepared in relatively short production cycles.

The invention will now be further described with reference to the following examples, however, without restricting its scope.

In the examples the following low molecular weight polymers, supplied by Hercules and identified by their trademarks, have been used:

- "KRISTALEX" 3115, that is a water-clear, highly colour stable, apolar copolymer having an M_n of respectively 1200, and that is largely derived from alpha-methylstyrene and styrene monomers, and
- "PICCOLASTIC A5", a viscous liquid mixture of oligomers (trimers and tetramers) of styrene having an M_n of 360.

Besides, GMS, (glycerol mono-stearate) a conventional coating agent whose function it is to prevent agglomeration and static of the expandable beads, is used.

The plasticizers have been studied in EPS for their expandability-strength balance with respect to regular grade EPS (having an M_w of about 175,000) and high strength grade EPS (having an M_w of about 200,000).

Examples 1 to 4, Comparative examples A to G

Samples of the EPS grades were prepared by polymerization carried out in a bench-scale (9-litre) reactor.

The plasticizer (loading calculated on the sum of styrene monomer and plasticizer) was first mixed with all the styrene at 50 °C for 30 minutes to achieve dissolution. Demineralised water was next poured into the reactor. Thereafter, polymerization was initiated by radicals of di-benzoyl peroxide (BPO) and t-butyl peroxybenzoate (tBP). The concentration of initiators was calculated on the styrene monomer only. Beads of particle size of 0.7-1.2 mm were made using about 0.05 %wt, calculated on the total amount of styrene and plasticizer, of bentonite and gelatine stabiliser. The blowing agent, pentane, was dosed during the polymerization reaction. The polymerization time for the regular grade EPS was about 210 minutes, whereas the polymerization time for the high strength grade EPS was about 230 minutes, both at 90 to 130 °C.

The raw beads so prepared were tumbled in a ribbon blender (a Hermann Linden machine for 1 kg batches, run for 10 minutes) with a coating composition comprising GMS until an uptake of 4 g (0.4 %wt) was achieved.

The coated beads were pre-expanded in a batch pre-expander (of the firm Händle) using a steam pressure of 0.20 bar gauge. The pre-foam-density reached after 25 seconds (D_{25}) and the steaming time required to achieve a density of about 20 g/l (t_{20}) were determined. The pre-expanded beads were allowed to mature overnight in an air-permeable silo and were machine moulded into

tiles of 300 mm by 300 mm by 50 mm in a steam-heated enclosed mould operating at 0.6 bar gauge. The pressure-decay time for each tile was noted. Next, the tiles were dried for two days at 70 °C and then conditioned and tested for cross-breaking strength (at break).

From Table 1 it follows that plasticizers improved the expandability as D_{25} and t_{20} were reduced in respect of the reference samples (Comparative examples A and G). Referring to Examples 1 to 4, the relative improvement in cross-breaking strength at lower steam pressures (0.6 bar gauge) in respect of Comparative example G, however, was much larger than that achieved with the use of plasticizer in Comparative examples B to E over reference sample A. Use of a plasticizer in high strength grade EPS still provides an acceptable pressure-decay time. On the other hand, referring to Comparative example F (in accordance with US-A-4,525,484) high cross-breaking strength is obtained, however, at the cost of the pressure-decay time.

Table 1

EXAMPLE	A	B	C	D	E	F[2]	G	1	2	3	4
Ingredients											
EPS grade (M_W of ±175,000)	+	+	+	+	+	+					
EPS grade (M_W of ±200,000)							+	+	+	+	+
A5 (%)	-	0.3	0.9	1.2	2.0	-	-	0.5	1.0	1.5	2.0
3115 (%)	-	-	-	-	-	1.5	-	-	-	-	-
Pentane in raw beads (%wt)	6.1	6.2	6.3	6.3	n.d.[3]	6.6	6.1	n.d.[3]	6.4	n.d.[3]	6.2
Property											
D_{25} (g/l)	20.0	18.3	16.2	16.0	15.1	16.8	21.8	20.7	18.7	n.d.	14.6
t_{20} (sec)	25.0	22.5	19.5	21.0	20.0	21.0	28.0	25.0	22.5	20.0	17.0
Preroam density (g/l)	20.0	19.9	19.6	18.5	17.8	21.0	20.5	20.7	19.8	20.0	20.2
Rel. cross-breaking strength at 0.6 bar g steam pressure[1] (N)	(1028)	152	142	146	46	130	(958)	299	274	297	290
Pressure-decay time (s)	117	245	275	244	224	398	39	187	267	263	240

1 corrected to a density of 20 g/l, and relative to sample A respectively G (absolute strength in brackets)

2 US-A-4,525,484

3 not determined, about 6.2 %wt

C L A I M S

1. Expandable beads based on a polymer of a vinylaromatic compound having a weight average molecular weight (M_w) in the range of 180,000 to 500,000 and containing a blowing agent and a plasticizer in an amount of 0.1 up to 4 %wt (as calculated on the total weight of the beads), wherein the plasticizer is an oligomer of styrene and/or alpha-methylstyrene having a number-average molecular weight (M_n) in the range of 200 to 2,000.

2. Expandable beads as claimed in claim 1, wherein the expandable beads are based on polymers of styrene and/or alpha-methylstyrene.

3. Expandable beads as claimed in claim 1 or 2, wherein the expandable beads are based on polystyrene.

4. Expandable beads as claimed in any one of claims 1 to 3, wherein the plasticizer has an M_n in the range of 200 to 1,200.

5. Expandable beads as claimed in claim 4, wherein the plasticizer has an M_n in the range of more than 500 to 900.

6. Expandable beads as claimed in any one of claims 1 to 5, wherein the expandable beads contain 5.0 to 12 %wt of blowing agent.

7. Expandable beads as claimed in any one of claims 1 to 5, wherein the expandable beads contain 3 to 4.9 %wt of blowing agent.

8. A process for preparing expandable beads as claimed in any one of claims 1 to 7, by polymerising the vinyl-aromatic compound in aqueous suspension in the presence of the plasticizer and adding the blowing agent to the suspension before, during and/or after the poly-

merisation.

9. Articles of expanded beads of a polymer of vinylaromatic compounds, obtainable by expanding and fusing the beads claimed in any one of claims 1 to 7.